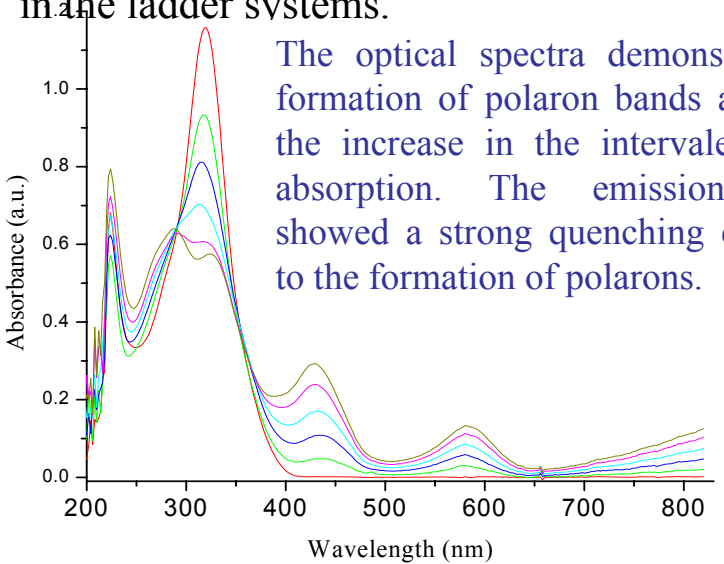
Delocalization in Novel Ladder Triarylamine Systems

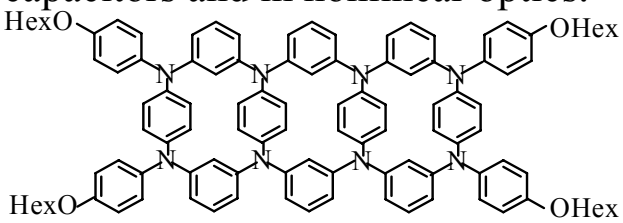
T. Goodson III, Wayne State University, DMR-0134691

Two ladder structures, bis-tetraazacyclophane and tris-tetraazacyclophane (tris-TCP), have been investigated in order to probe the effect of electron delocalization along the frame of the molecular architecture. This project was carried in collaboration with Professor John Hartwig at Yale University. The electronic and spectral properties were conducted on neutral and oxidized forms of these systems and are compared to the linear building block molecule. This methodology was similar to our previous investigations with triarylamine dendrimer systems. Our most results suggest the generation of stable delocalized polarons in the ladder systems.

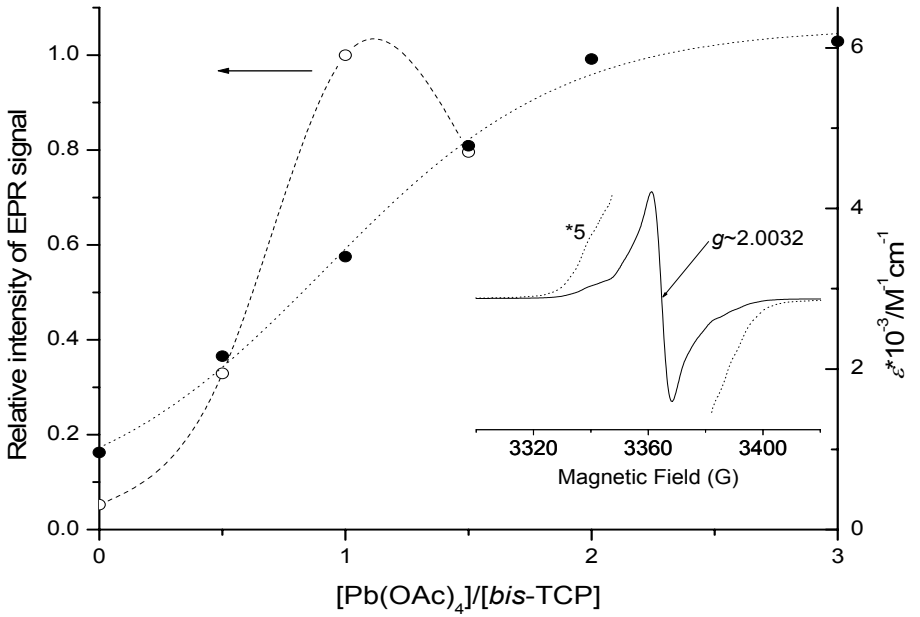


The optical spectra demonstrated the formation of polaron bands as well as the increase in the intervalence band absorption. The emission spectra showed a strong quenching effect due to the formation of polarons.

Electron paramagnetic resonance spectra suggest that polarons generated by chemical oxidation of the ladder systems are highly delocalized and strongly coupled. An ultrafast fluorescence decay profile was observed for the ladder systems. These properties suggest that there is strong polaron delocalization which may be useful in novel applications of capacitors and in nonlinear optics.



tris-TCP



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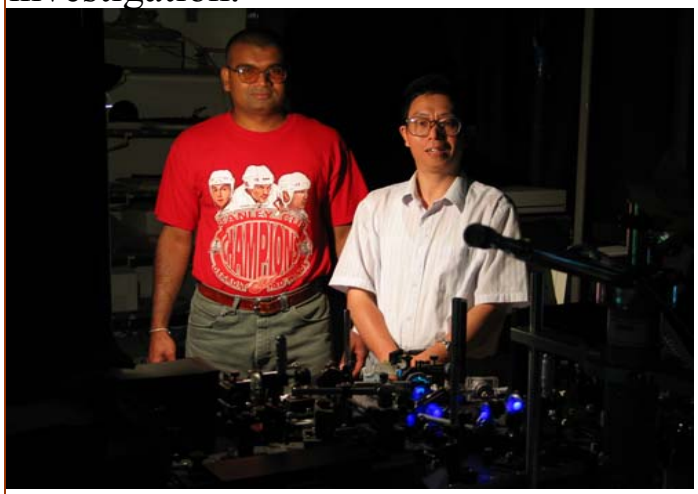
Educational Aspects of Study:

Graduate Student Mahinda Ranasinghe and Postdoctoral Fellow Xinzhong Yan have worked on this project. The triarylamine ladder systems were synthesized by Professor John Hartwig's group and his graduate student J. Pawlas. The project incorporated a number of spectroscopic tools that these two scientists from the PI's group have used thoroughly. While more sophisticated measurements were utilized such as time-resolved absorption and emission as well as 3-pulse photon echo measurements, other methods that were more familiar to the summer students that worked with the two scientists in our group. This included EPR and electrochemical measurements as well as steady-state absorption and emission measurements. This allowed for the students (undergraduate and high school) to first contribute to this project with techniques that they were already familiar with and gave them the time to understand the more sophisticated and less familiar techniques.

Outreach Activities:

The PI's group participated in the project SEED (ACS) program. Funding from NSF through this project has allowed for at lease one summer student each year for five years now. The summer students trained under experienced graduate (Mahinda Ranasinghe) and postdoctoral (Xingzhong Yan) scientists. This years summer student was Valedictorian of Northwestern High School in Detroit and will be attending Wayne State University in the fall. Mr. Hussein has already learned the fundamentals of EPR, E-chem., steady state, and time-resolved optical techniques during this investigation.



M. Ranasinghe (left) and X. Yan (right) stand before the fluorescence up-conversion unit in studies of ultra-fast photo-physics of novel Ladder systems.